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The Solvent Influence on Some Physicochemical Properties of $Cu(NO_3)_2·3H_2O–(CH_3)_2SO$ Solutions

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Abstract—The electrical conductance of $Cu(NO_3)_2·3H_2O$ solutions (0.00886–2.82 mol L^{-1}) in dimethylsulfoxide at 288–318 K has been studied by conductometry.

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Aqueous solution of copper(II) nitrate acidified with nitric acid attracts attention as an electrolyte for copper plating at increased current density (up to 100 A dm^{-2} [1]). The coatings thus obtained do not contain nonmetal inclusions and are highly conductive [2].

The electrical conductance of aqueous copper(II) nitrate solutions as functions of their concentration has a maximum. The limiting molar conductance of the copper(II) ions [$\lambda_0(1/2Cu^{2+}, H_2O, 298\ K) = 56.6\times 10^{-4}\ S\ m^2\ mol^{-1}$] is significantly lower than that of nitrate ions [$\lambda_0(NO_3^-, H_2O, 298\ K) = 72\times10^{-4}\ S\ m^2\ mol^{-1}$] [3] due to enhanced hydration of the double-charged metal ions. Consequently, the diffusion coefficient of anions is more than two times higher than that of the copper(II) ions [3]: $D(1/2Cu^{2+}, H_2O, 298\ K) = 0.75\times10^{-9}\ m^2\ s$, $D(NO_3^-, H_2O, 298\ K) = 1.92\times10^{-9}\ m^2\ s^{-1}$.

Dimethylsulfoxide DMSO and water are miscible at any ratio. Small amount of water (up to 10 mol %) practically does not influence the conductivity of solutions in DMSO [4]. DMSO molecules can bind the metal ions via oxygen of sulfur atoms. The oxygen atom of DMSO is non-polarizable, thus DMSO is a hard base. Thus, the Cu^{2+} (hard acid) solvation in DMSO occurs via the oxygen atom [5].

In this work the solubility of $Cu(NO_3)_2·3H_2O$ in DMSO was determined. The results of conductometric studies of these solutions at are presented.

The conductance of $Cu(NO_3)_2·3H_2O$ solutions in DMSO at 288 K rapidly increased with increasing salt concentration up to 0.4 mol L^{-1} (Fig. 1, curve *1*). Further increase in the salt concentration led to a steady decrease in the conductance down to a certain limiting value. At higher concentrations (above 1.4 mol L^{-1}), the measurements reproducibility was poor.

Upon increasing temperature to 318 K (Fig. 1, curves *2*–*5*), the mobility of electrolyte ions was enhanced, and the solutions conductance increased. The σ maxima at the concentration dependence were somewhat shifted towards higher concentrations. At 318 K the experimental data points scatter increased even at lower concentration, due likely to breaking of

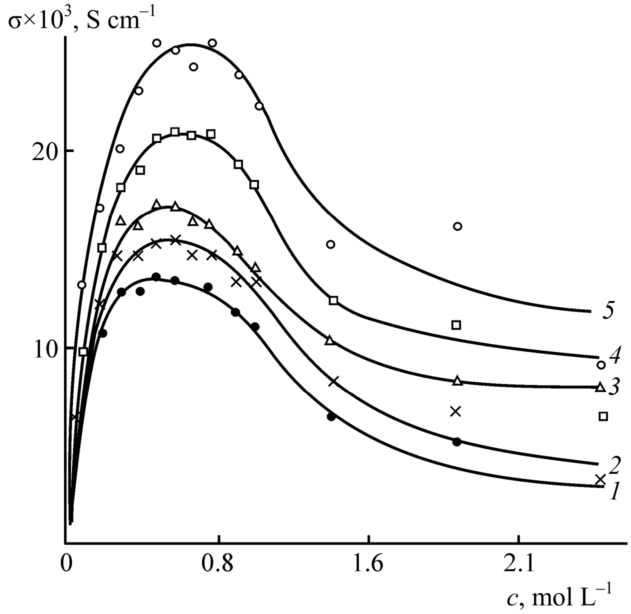

Fig. 1. Specific conductance (σ) as a function of concentration at different temperatures, K: (*1*) 288, (*2*) 293, (*3*) 298, (*4*) 308, and (*5*) 318.

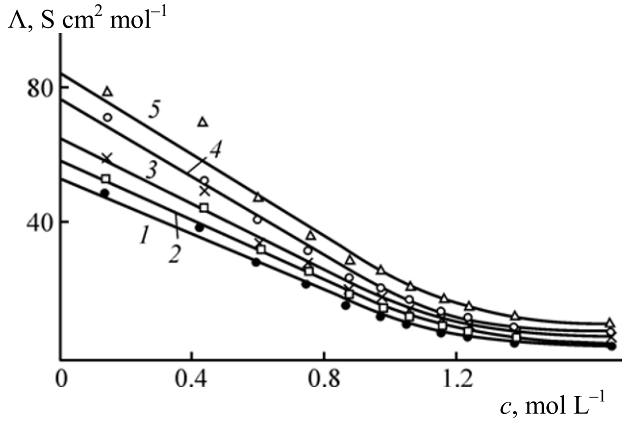

Fig. 2. Molar electrical conductivity (Λ) as a function of concentration at different temperatures, K: (*1*) 288, (*2*) 293, (*3*) 298, (*4*) 308, and (*5*) 318.

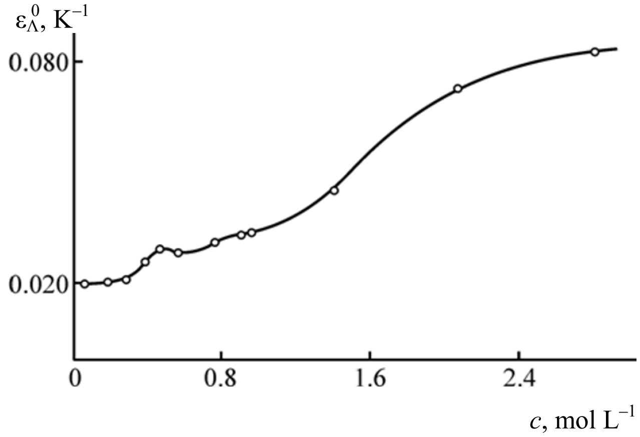

Fig. 3. Relative temperature coefficient of electrical conductance (ε_Λ) as a function of $Cu(NO_3)_2 \cdot 3H_2O$ concentration in DMSO.

the intermolecular hydrogen bonds that occurred between molecules of $(CH_3)_2SO$ and H_2O (from crystal hydrate) at lower temperature. The decrease in the conductance in the case of concentrated solutions could be attributed to by ions association and high solutions viscosity.

The molar electrical conductance $\Lambda[1/2Cu(NO_3)_2 \cdot 3H_2O$, DMSO, $T]$ as a function of the salt concentration followed the Kohlrausch root square law at all studied temperatures when the concentration of salt did not exceed 0.5 mol L^{-1} (Fig. 2). With increasing temperature, the slope of the linear part of the plot increased, and the reproducibility of experimental points became poorer. By means of the Fuoss-Krauss method, the limiting molar electrical conductance was estimated and the association constants were calculated from the electrical conductance data (Table 1).

Table 1. Limiting molar conductance (Λ_0) and ionic conductance (λ_0) of $Cu(NO_3)_2 \cdot 3H_2O$ solutions in DMSO as a function of temperature, association constant (K_{as}), and the temperature coefficients of electrical conductivity [$\varepsilon_\Lambda^0 = (\partial \ln \Lambda_0/\partial T)_c$]

T, K	Λ_0, S cm^2 mol^{-1}	ε_Λ^0, K^{-1}	$\lambda_0(1/2Cu^{2+})$	$\lambda_0(NO_3^-)$	K_{as}
			S cm^2 mol^{-1}		
288	53.84		30.02	22.24	13.51
293	58.94		32.92	24.39	6.05
298	63.44	0.0214	36.44	27.00	10.64
303	–		40.34	29.89	–
308	76.92		44.24	32.78	5.83
313	–	0.0087	46.16	34.20	–
318	83.64		48.09	35.63	9.25

The relative temperature coefficient of electrical conductance as a function of the solution concentration was also of interest. In the diluted solutions (below 0.3 mol L^{-1}) of copper(II) nitrate in DMSO, the average temperature coefficient of electrical conductance at 288–308 K, 0.0216 K^{-1}, was of the same order of magnitude as ε_Λ^0; at 308–318 K it decreased to 0.0190 K^{-1}. When the copper salt concentration in the solution increased the ε_Λ value grew following the curve with extremes (Fig. 3), evidently due to the enhanced interaction of the solution components and to the enlargement of the associates. The maxima on the plots of relative temperature coefficient of electrical conductance as a function of the solution concentration revealed the chemical interaction of the components, the corresponding solution concentration indicating the composition of the formed compounds [7].

The first and the second maxima on the plots (Fig. 3) corresponded to the molar ratios of $[Cu(NO_3)_2]$:$[H_2O]$:$[(CH_3)_2SO]$ of 1:3:28 and 1:3:14, respectively. The formation of stable homomolecular aggregates of 13 DMSO molecules was previously proved experimentally [8]. These aggregates could be preserved also in the presence of the dissolved electrolyte.

As seen from Table 1, in DMSO solutions the mobility of Cu^{2+} was higher than that of NO_3^-. However, the mobility of Cu^{2+} was lower than that of

NO_3^- when in aqueous medium. In the aqueous media the mobility of copper(II) ions was noticeably higher than that in the organic media. All the above-stated observations were due to the enhanced solvation of the copper nitrate ions in DMSO and the increased solutions viscosity.

By using the Nernst equation $D_i = RT\lambda_0^i|z_i|^{-1}F^2$ and the expression of the diffusion coefficient as $D = (z_+ + |z_-|)D_+D_-(\Sigma z_iD_i)^{-1}$ (with D_i being the ions diffusion coefficient, other parameters having the usual meaning), the diffusion coefficients D_i and D were determined at different temperatures, and the relative temperature coefficients of the diffusion coefficients $\varepsilon_D = (\partial \ln D_i/\partial T)_c$ were calculated (Table 2).

Comparison of the data in Table 2 and the respective data for aqueous solutions revealed the decrease in the ions mobility in DMSO in the absence of the external electrical field.

The particles formed in the DMSO solution due to Cu^{2+} solvation were larger than the $[(CH_3)_2S(O)NO_3]^-$ adducts, thus the temperature coefficient of the metal ions diffusion at 288–308 K was higher.

The weakening of the hydrogen bonding between the molecules in the solution above 293 K seemingly affected more the cations complexes than the anions adducts. Consequently, at 308–318 K the decrease in

Table 2. Diffusion coefficients (D) of $Cu(NO_3)_2$, Cu^{2+}, and NO_3^- in DMSO at different temperatures and thermal diffusion coefficients (ε_D) of the same ions

T, K	$D\times10^5$, cm^2 s^{-1}			ε_D, K^{-1}	
	$Cu(NO_3)_2$	$1/2Cu^{2+}$	NO_3^-	$1/2Cu^{2+}$	NO_3^-
288	0.472	0.373	0.545		
293	0.547	0.432	0.631	0.0398	0.0326
298	0.623	0.492	0.719		
308	0.807	0.670	0.900	0.0104	0.0211
318	0.941	0.740	1.090		

Table 3. Dissociation degree (α) and dissociation constant (K_d) of $Cu(NO_3)_2\cdot3H_2O$ in DMSO at different concentrations and temperatures

c, mol L^{-1}	$\alpha = \Lambda\cdot\Lambda_0$					$K_d = \Lambda^2\cdot c/\Lambda_0\cdot(\Lambda_0–\Lambda)$				
	288	293	298	308	318	288	293	298	308	318
0.009	0.93	0.91	0.93	0.94	0.93	0.1105	0.0867	0.1083	0.1330	0.1013
0.094	–	0.77	0.79	0.70	0.84	–	0.2517	0.2705	0.1554	0.4116
0.18	0.56	0.58	0.54	0.55	0.57	0.1321	0.1461	0.1174	0.1224	0.1349
0.28	0.43	0.45	0.45	0.43	0.43	0.0902	0.1053	0.1051	0.0926	0.0921
0.38	0.32	0.34	0.33	0.33	0.36	0.0575	0.0647	0.0618	0.0629	0.0778
0.47	0.27	0.28	0.29	0.29	0.33	0.0484	0.0522	0.0545	0.0576	0.0734
0.56	0.23	0.24	0.24	0.25	0.27	0.0377	0.0429	0.0429	0.0468	0.0547
0.66	–	0.19	0.19	0.21	0.22	–	0.0302	0.0310	0.0351	0.0403
0.75	0.16	0.17	0.17	0.19	0.20	0.0244	0.0258	0.0262	0.0316	0.0384
0.90	0.13	0.13	0.13	0.14	0.16	0.0162	0.0169	0.0173	0.0215	0.0268
1.00	0.10	0.12	0.11	0.12	0.12	0.0124	0.0153	0.0135	0.0169	0.0200
1.40	0.043	0.05	0.06	0.06	0.06	0.0028	0.0038	0.0049	0.0050	0.0062
2.07	0.023	0.03	0.03	0.04	0.04	0.0012	0.0016	0.0020	0.0029	0.0048
2.82	0.008	0.009	0.01	0.015	0.02	0.00022	0.0002	0.0003	0.0006	0.0010

ε_D ($1/2Cu^{2+}$) was more pronounced than that of ε_D (NO_3^-) value.

The electrolytic dissociation degree of copper(II) nitrate in DMSO medium as derived from the electrical conductivities ratio $\alpha = \Lambda/\Lambda_0$ equaled 0.93 in the diluted solution (0.01 mol L^{-1}) (Table 3), and was not much affected by temperature. The increase in the copper salt concentration was accompanied by increasing concentration of water. Due to the formation of the heteromolecular associates $H_2O\cdots(CH_3)_2SO$ in the solution, the degree of the electrolyte ions solvation decreased, and the solutions viscosity grew [9]. As a result, the association of Cu^{2+} and NO_3^- with the formation of ion pair (or may be associates of three ions) was facilitated. Thus, the increase in the solutions concentrations at constant temperature led to the decrease in the electrolyte degree of dissociation (Table 3).

The influence of temperature (especially above 293 K) on the degree of dissociation of copper(II) nitrate in DMSO solutions was noticeable in the case of concentrated solutions.

The dissociation constant of copper(II) nitrate in the examined solutions, as determined from the dilution law (Table 3), was significantly changing with the increase in the electrolyte concentration. The influence of temperature on the dissociation constant as well as on the degree of dissociation was most noticeable at 308–318 K. The changes of the dissociation constant clearly proved the enhancement of the ionic interaction with the increasing solution concentration. The increase in the dissociation constant was in line with the decrease in the ions association constant (Table 1).

The following scheme of the ions state in the solutions of $Cu(NO_3)_2{\cdot}3H_2O$ in DMSO could be generalized from the ions transport data. In pure DMSO, the aggregates of 13 molecules were formed, stable at room temperature. Due to weak bonds holding the aggregates together they were disrupted at 35°C. The tiny amounts of copper(II) nitrate crystal hydrate were completely dissociated when dissolved in DMSO. Water molecules formed the stable solvates $H_2O\cdots(CH_3)_2SO$. With increasing salt concentration, the ratio of the solvent molecules decreased. The deficiency of the solvent molecules for the ions solvation was due to the electrolyte concentration increase as well as to increase in the water amount from the crystal hydrate. Bonding to $(CH_3)_2SO$, water molecules induced the breaking of the organic homomolecular associates; at the same time, the stronger heteromolecular associates were formed, thus giving rise to the solution viscosity increase. As the electrolyte concentration increased, the solvation number of Cu^{2+} (and probably that of NO_3^-) decreased; as a result, starting from the 0.4 mol L^{-1} solution, the copper(II) and nitrate ions were associated at 288 K, and the solution electrical conductivity decreased. Further increase in the electrolyte concentration led to the decrease in the conductivity.

The increase in temperature led to the increase in the ions mobility and thus enhanced the solution conductivity; at the same time the maximum of the conductivity as a function of concentration was shifted to somewhat more concentrated solutions.

EXPERIMENTAL

The solutions conductivity was measured with OK-102/1 conductometer. The constant of the conductometer cell was estimated with 0.1 mol L^{-1} KCl solution as a reference. During measurement, the cell temperature was maintained within ±0.5 K with UTU-4 ultrathermostat. The salt crystal hydrate was prepared as described in [9] and purified by recrystallization from aqueous solution. DMSO of the chemical pure grade was distilled under a reduced pressure (n_D^{25} 1.4816).

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